

MODELLING OF REACTIVE DISTILLATION COLUMN BY USING MOSAIC

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
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JUNE 2014

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ABSTRACT

Due to many advantages of reactive distillation column (RD) comparing to traditional method (reactors follows by distillation columns) in chemical synthesis, RD has been drawing attentions of researchers around the world to explore its potentials in chemical industries.

Modelling of RD can be made by many different modelling environments such as Matlab, Fortran and so on. However, it is a time consuming process and a lot of effort will be required in order to get the solutions of the model. Since the modelling is done by using their own programming languages, it has the poor readability. Thus, users prone to make the mistakes during coding and error identification will be difficult by using these modelling software.

In this study of RD modelling, a new modelling environment called MOSAIC will become the focus. MOSAIC is a web based modelling software and it introduces the new modelling approach in order to overcome what it seems as insufficient places of other modelling software. The key features of MOSAIC include modelling in the documentation level, reuse of model elements, code generation for other modelling environments and centralized cooperation on internet. (Kuntsche, Barz, Kraus, Arellano-Garcia, & Wozny, 2011)

Modelling of reactive distillation column is based on the steady state equilibrium model. It is assumed that the liquid and vapour phase behave ideally. Steady state equilibrium model can be described by MESH equations. MESH equations are material balance equation, phase equilibrium equation, summation equations and energy balance equation.

From the results, it can be seen that almost 100% conversion of reactants are achieved with 94% of MTBE purity. The temperature profile shows that the temperature is maintaining at 354K from condenser to feed stage. This is due to high purity of n-butene in each stages. After feed stage, the temperature increases rapidly until it reaches highest temperature of 424K at reboiler stage. This is caused by high mole fraction of MTBE from condenser to reboiler stage.

MOSAIC makes the modelling possible even without the knowledge of programming language. Latex documentary language is used by MOSAIC in documentation of modelling equations. High readability of Latex allows modelling using MOSAIC to be less errors and without much effort.

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NOMENCLATURE

a	Activity	-
F	Feed molar flow rate	mol/s
H	Enthalpy	J/mol
L	Liquid molar flow rate	mol/s
M_j	Molar liquid hold up on stage j	mol/s
P	Total pressure	Pa
P^o	Saturated vapour pressure	Pa
R	Reaction rate	mol/s
r	number of reactions	-
t	time	s
T	Temperature	K
V	Vapour molar flow rate	mol/s
W	Catalyst weight	kg
x	Liquid composition	-
y	Vapour composition	-
z	Feed composition	-

Greek letters

δ	Parameter for reaction occurrence on stage j (0 or 1)	-
ϕ	Fugacity coefficient	-
γ	Activity coefficient	-

Subscripts

i	Component number
j	Stage number

Superscripts

c	Total number of components
-----	----------------------------

List of abbreviations

EQ	Equilibrium model
MeOH	Methanol
MTBE	Methyl tert-butyl ether
NEQ	Non-equilibrium model
RD	Reactive distillation

Chapter 1: Introduction

1.1 Motivation and statement of problem

RD technology has brought many advantages in chemical production, these include heat integration, elimination of azeotropes, 100% conversion of reactants with suppression of side products and lower capital cost. Although not all the chemical manufacturing are suitable by using RD, there are still a lot opportunity in application of RD technology in chemical industries. The production of MTBE is one of chemical processes can be fully benefited from RD technology.

The equation oriented modelling of RD has been done by many researchers by using different modelling environments, these include Matlab, FORTRAN and so on. Modelling of complex models will be time consuming process and it requires a lot of efforts especially to correct the errors during the coding. Besides that, modelling using of Matlab will experience the problem of readability since it is written based on its own programming language. Hence, it tends to cause modelling process to be difficult and frustrating. Other tools for the solution of models will be AspenPlus. Although the simulation can be done easily by using AspenPlus, it lacks in transparency of equations systems involved and it will never meet the requirement when a customized model is needed.

MOSAIC is a new modelling environment and it brings the new modelling approach. It is designed for minimization of modelling errors, minimization of programming effort, avoidance of errors and effort in documentation and encouragement of cooperative work. Some of the key features of MOSAIC are modelling in the documentation level, reuse of model elements, code generation for other modelling environments and centralized cooperation on internet. Furthermore, just like Matlab, it is designed to build a customized model as well. (Kuntsche et al., 2011)

1.2 Objective and Scopes

The objective of the research is to

- Explore the modelling of RD for MTBE production by using MOSAIC

1.3 The scopes of the research are

- Modelling of equilibrium(EQ) model of RD by using MOSAIC based on the given parameters of MTBE production
- Validation of the modelled RD with results from literature.
- Comparison between MOSAIC and other modelling environments.

Chapter 2: Literature Review

2.1 Reactive Distillation Column

2.1.1. General Introduction of RD

Although reactive distillation column (RD) was invented in 1921, the industrial application is only started to after 1980's. (Agreda, Partin, & Heise, 1990) RD consists of both reactor and distillation column under a single vessel. It have brought many advantages to chemical production especially for its high conversion and selectivity. Production of MTBE is one of chemicals that can be fully benefited from RD technology. However, not all the chemical production are suitable to use RD in manufacturing.

The introduction of in-situ reaction with distillation in a single vessel leads to the complex interactions between vapour- liquid equilibrium, vapour-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed process) and chemical kinetics. (Taylor & Krishna, 2000) This makes the design of these systems to be difficult.

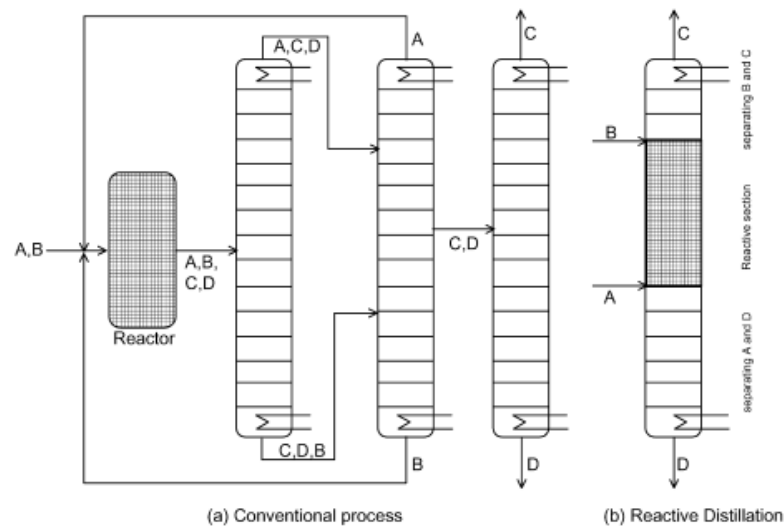


Figure 1:(a) Typical configuration of a conventional process consisting of a reactor followed by a distillation train. (b) The reactive distillation configuration. (Stichlmair & Frey, 1999)

From the Fig. 1(a), it shows the traditional method of chemical synthesis where the chemical reaction occurs in reactor and then the products are separated by distillation train. If the azeotropes are formed by the products, it will cause the separation of chemical components to be difficult and the distillation train will far more complicated than one shown in the figure above.

From the Fig. 1(b), the RD column consists of a reactive section in the middle with nonreactive rectifying and stripping sections at the top and bottom. For a properly designed RD column, virtually 100% conversion can be achieved. (Taylor & Krishna, 2000)

2.1.2. The advantages of RD

The RD is quite beneficial especially for the exothermic reaction. MTBE production is one of the exothermic reaction. The heat integration allows fully taking advantage of heat energy released from the chemical reaction. The heat released will be used in vaporization and reduce the duty of the reboiler. This will further decrease the risk of runaway reaction.

In addition, the formation of azeotropes can be avoided in RD. For the case of MTBE, by using traditional method where the reactor followed by distillation columns, extra 10% of methanol is required to feed into the reactor in order to reduce the mainly isobutylene dimers by-product formation. (Elkanzi, 1996) The MTBE produced forms the azeotropes with the methanol and isobutylene. The reactant mixture leaving the reactor forms three minimum azeotropes (Taylor & Krishna, 2000) and it causes the separation of the mixture to be difficult. However, with the RD concept, it allows some of the azeotropes just “reacting away”. (Doherty & Buzad, 1992)

Moreover, the conversion of reactants can nearly achieve 100% with the suppression of the side reactions in RD. Thus, the selectivity of product is high. The limitation of chemical equilibrium can be overcome by RD by removing the product from reacting mixture. Therefore, the complete conversion can be achieved with the shifting of equilibrium to the right. For the case of MTBE, nearly 100% of conversion of isobutylene and methanol can be achieved along with suppression of the formation of the unwanted dimethyl ether by using RD. (Sundmacher, 1995)

Furthermore, the capital cost of RD in industrial production is lower than conventional method. The high number of required distillation columns can be avoided by using RD. The reduction of required pumps, instruments and piping also further decrease the capital cost. (Mohammed, 2009)

2.1.3. The constraints of RD

Although RD is a new technology and brings many advantages to the production of MTBE, not all the chemicals manufacturing are suitable by using RD. There are few constraints of RD. (Towler & Frey, 2002) The constraints could be the reactants and products may not have suitable volatility to maintain high concentration of reactants and low concentration of products in the reaction zone. Moreover, if the residence time is too long, a large column size and large tray hold-ups will be needed. Therefore, it may be more economical to use conventional method of reactor followed by distillation columns. Besides that, the optimum temperature and pressure of the reaction may not suitable under the optimal conditions of distillation. Furthermore, scale up to large flow rate is not suitable by using RD due to liquid distribution problems in packed RD columns.

2.2 MTBE

2.2.1. Background of MTBE production

In 1998, the worldwide production MTBE had achieved its records high with 6.6 billion gallons annually (Ahmed, 2001), with the US occupied the large portion of it, around 4.3 billion gallons per year. Besides that, MTBE was considered as one of the top 50 chemicals produced in the world. (WHO, 1998) However, the use of MTBE in US as gasoline additive gradually replaced by the ethanol, as the legislation favouring the ethanol. This is due the underground water and soil contamination caused by MTBE. (EIA, 2003b) It is estimated to cost 1 billion to 30 billion dollars to clean the aquifers and municipal water supplies and replacing leaky underground oil tanks. (Napoli, 2004) Nevertheless, the demand of MTBE is still growing in Asia as ethanol is less subject to subsidies.

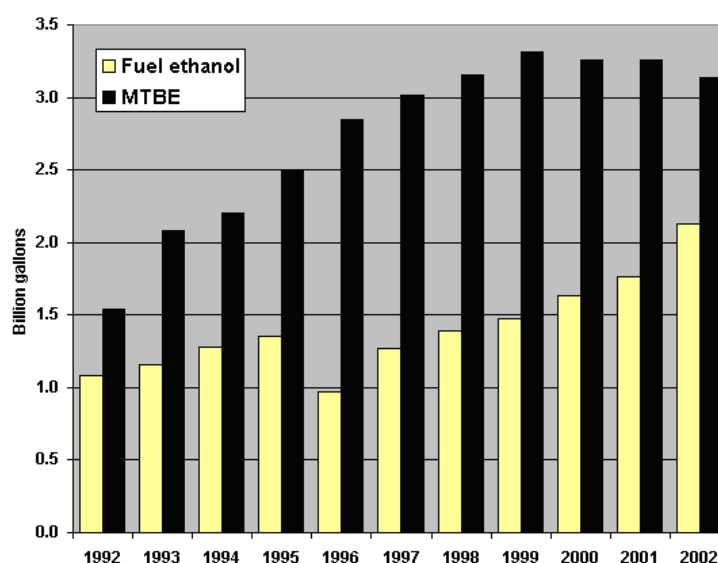


Figure 2: The bar chart shows the MTBE & ethanol production from 1992 until 2002 in US (EIA, 2003a)

Despite legislation of US in many states gradually phase out the use of MTBE as gasoline additive, worldwide MTBE production is still remains constant due to the growth in Asian markets. The information from GIA shows that global market MTBE is expected to reach 19.2 million tons by the year 2017, this is driven primarily by the increased demand from developing countries such as Asia, particularly China, Middle East, and Latin America. The increasing automobile ownership in these countries and use of MTBE

as an additive to improve quality of gasoline is expected to fuel consumption of MTBE. (GIA, 2011)

2.2.2. MTBE as Gasoline Additive

MTBE is widely used as the oxygenated compound in gasoline. The high oxygen content of MTBE will help in the complete combustion of the gasoline. In other words, with the sufficient amount of oxygen, the incomplete combustion of gasoline can be avoided and the released of carbon monoxide also can be eliminated. Besides that, another function of MTBE in gasoline is to increase the octane number of gasoline. MTBE is widely used as anti-knocking agent in gasoline to replace tetraethyl lead as gasoline additive. (Marceglia & Oriani, 1982) This is due to the environmental and health concerns of poisonous gas, lead and lead oxide which are released on combustion.

Other properties of MTBE such as low sulphur content, acceptable blending vapour pressure, high miscibility in gasoline, moderate boiling point, and stability in storage and lower cost compared to those of other high-octane components, made it the attractive choice as gasoline additive. (Ziyang, Hidajat, & Ray, 2001)

2.2.3. MTBE Synthesis

Traditionally, the MTBE is produced by the reaction between the methanol and isobutylene using the acid ionic exchange resins in fixed bed reactor at the operating temperature between 313 and 353 K and under the pressure of 200 psig in order to maintain the reaction in liquid phase. The reaction is reversible and exothermic. (Ziyang et al., 2001) The chemical reaction can be shown as below:



Normally, sulfonated acidic ion-exchange resin such as Lewatit SPC 118, Amberlyst 15 or Purolite CT-115 are used as catalyst in the reaction. (Ziyang et al., 2001) The isobutene can be taken from C4 streams of catalytic cracking processes for gasoline production and of ethylene manufacture. While the methanol is extensively produced by number of firms

from inexpensive natural gas and other carbon sources. (Mitani, Keller, Bunton, Rinker, & Sandall, 2002)

2.3 *Equilibrium Model of RD*

2.3.1. *RD Models*

There are several models in designing of RD. (Richard Baur, 2000) They are listed as follows:

1. Steady-state equilibrium (EQ) stage model
2. Dynamic EQ stage model
3. Steady-state EQ stage model with stage efficiencies
4. Dynamic EQ stage model with stage efficiencies
5. Steady-state non-equilibrium (NEQ) stage model, where the interphase mass transfer is described by rigorous Maxwell-Stefan diffusion equations
6. Dynamic NEQ stage model
7. Steady-state NEQ cell model, developed by Higler (1999), in order to account for staging of the vapour and liquid phases during cross-current contacting on a distillation tray

In this study, modelling of RD by using MOSAIC will be based on steady state EQ model. In equilibrium (EQ) stage model, the vapour and liquid phases are assumed to be in thermodynamic equilibrium. (R Baur, Higler, Taylor, & Krishna, 2000)

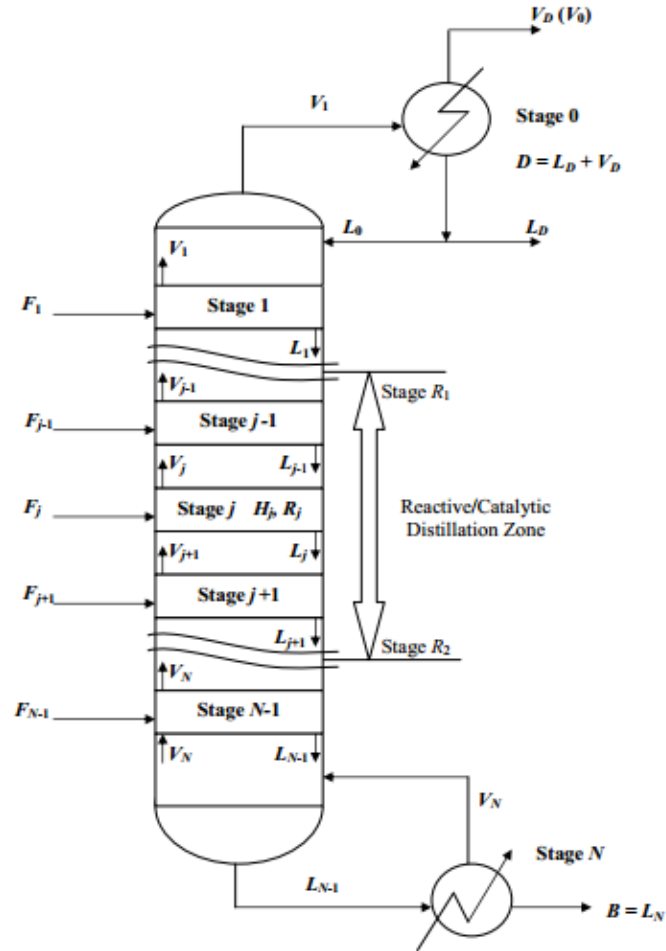


Figure 3: Schematic Representation of a Reactive Distillation Columns (Murat, Mohamed, & Bhatia, 2003)

2.3.2. Mathematical Modelling of EQ Model

The first step of modelling begins with mathematical modelling by formulation of equations to describe processes occurring in RD at the steady state. These formulated equations or just MESH equations will be required in finding solution of the model. The letters of MESH stand for material balance equations, phase equilibrium equations, summation equations and heat balance equations. The MESH equations shown below are modified from work of Murat et al. (2003).

Material balance equations

The material balance of every stages of RD can be represented by equation as follow:

Overall material balance

$$\frac{dM_j}{dt} = F_j - L_j - V_j + V_{j+1} + L_{j-1} + \delta_j R_j$$

Components material balance

$$\frac{dM_j x_{j,i}}{dt} = F_j z_{j,i} - L_j x_{j,i} - V_j y_{j,i} + V_{j+1} y_{j+1,i} + L_{j-1} x_{j-1,i} + \delta_j \sum_{r=1}^R (v_{i,r} r_{j,r})$$

Since the model is assumed as steady state, and thus the derivative of material balance will be equal zero. Both j and i are subscripts to represent the stages numbers and components respectively. F represents feed flow rate, L represents liquid flow rate then V will represent vapour flow rate. x and y are the mole fraction of liquid and vapour respectively.

Furthermore, for integrated reactive part of equation, r represents the reaction rate and v represents the stoichiometry of chemical components. The value of δ will be either 0 or 1 to decide whether reaction occurring at the stages or not.

Phase equilibrium equations

$$y = \frac{\gamma P^o x}{\phi P}$$

Phase equilibrium relation equation describes the relationship between liquid mole fraction and vapour mole fraction of chemical components when vapour and liquid at equilibrium state. For the ideal condition, the value of activity coefficient, γ and fugacity, ϕ will be equal to 1. Saturated vapour pressure, P^o can be calculated using of Antoine equation and P is pressure of reactive distillation column.

Summation equations

$$\sum_i^c x_{j,i} = 1.0 \quad (\text{Liquid phase})$$

$$\sum_i^c y_{j,i} = 1.0 \quad (\text{Vapour phase})$$

From the summation equation, it states that sum of mole fraction of each components in liquid phase and vapour phase of each stages will be equal to 1.

Enthalpy balance equations.

The energy balance of each stages of RD can be described by equation as follow

$$\frac{dH_j}{dt} = F_j H^F + L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V - V_j H_j^V - \delta_j \sum_{r=1}^R (\Delta H_{j,r}^R) r_{j,r}$$

Again, for the steady state, the derivative of energy balance will be equal to zero. For the reactive part of the equation, ΔH is enthalpy change of chemical reaction, r is the rate of reaction and δ will decide whether the reaction taking place at each stages or not. For the case RD modelling for MTBE production, it assumes only a single reaction, and thus the summation of enthalpy change can be ignored.

2.4 Kinetics model of MTBE Production

For the production of MTBE, the kinetics model is obtained from work of Rehfinger and Hoffmann (1990) . The activity based rate model is shown as follow:

$$r_j = Wqk_f \left(\frac{a_i^{IB}}{a_i^{MeOH}} - \frac{a_i^{MTBE}}{K_{eq} a_i^{2MeOH}} \right)$$

where

$$a_i = \gamma_i x_i$$

$$k_f = 3.67 \times 10^{12} \exp\left(-\frac{11110}{T}\right)$$

$$K_{eq} = 284 \exp[f(T)]$$

$$f(T) = A_1 \left(\frac{1}{T} - \frac{1}{T_0} \right) + A_2 \ln \left(\frac{T}{T_0} \right) + A_3 (T - T_0) + A_4 (T^2 - T_0^2) + A_5 (T^3 - T_0^3) + A_6 (T^4 - T_0^4)$$

$$T_0 = 298.15 \text{ K}$$

$$A_1 = -1.49277 \times 10^3 \text{ K}$$

$$A_2 = -77.4002$$

$$A_3 = 0.507563 \text{ K}^{-1}$$

$$A_4 = 9.12739 \times 10^{-4} \text{ K}^{-2}$$

$$A_5 = 1.10649 \times 10^{-6} \text{ K}^{-3}$$

$$A_6 = -6.27996 \times 10^{-10} \text{ K}^{-4}$$

From the equation, W is weight of catalyst of each stages. q is the amount of acid groups on the resin per unit mass with value of 4.9 equiv/kg. The activity of each components is the product of its activity coefficient and liquid mole fraction. k_f is reaction rate constant and K_{eq} is equilibrium constant.

2.5 MOSAIC

2.5.1. Introduction of MOSAIC

MOSAIC is a web-based modelling software which brings the new modelling approach. It makes the modelling possible without knowing the programming language of modelling. It is designed for minimization of modelling errors, minimization of programming effort, avoidance of errors and effort in documentation and encouragement of cooperative work. (Kuntsche et al., 2011)

2.5.2. 4 Main Features of MOSAIC

One of the important features of MOSAIC is modelling at the documentation level. It means that MOSAIC can make the modelling at documentation level without any paperwork. The equations can be documented easily by MOSAIC using Latex documentary language. By using Latex, the documented equations have the same readability as documentation level. In addition, modelling can be done by MOSAIC even without knowing of modelling programming languages.

Besides that, MOSAIC is also designed for reuse of model elements effectively. In MOSAIC, modelling is done by creating of objects separately. These objects include notation object, equation objects, function objects, equation system object, evaluation object and parameter object. Each objects can be reused by another models. Thus, it will reduce the effort of modelling.

The next important features of MOSAIC is code generation for other modelling environments. MOSAIC itself can be a code generator and solver. However, MOSAIC is not designed to be a full solver as complicated models cannot solved by using MOSAIC. MOSAIC has more complete support of code generation for other modelling environments.

Moreover, MOSAIC also has the feature of centralized cooperation on internet. It allows users to share their models easily. The shared model can be read or write by another user on internet.

2.6 *Summary*

By introduction of RD technology in chemical industries, it brings numerous advantages by comparing with traditional chemical synthesis method. MTBE production is one of the chemical synthesis that can be fully benefited from RD technology. Those advantages include heat integration, elimination of azeotropes, 100% conversion of reactant with suppression of side products and the lower capital cost.

For the next chapter, procedure of modelling using MOSAIC based on the given parameters of MTBE production will be discussed.

Chapter 3: Methodology

3.1 Conditions of MTBE Production using RD

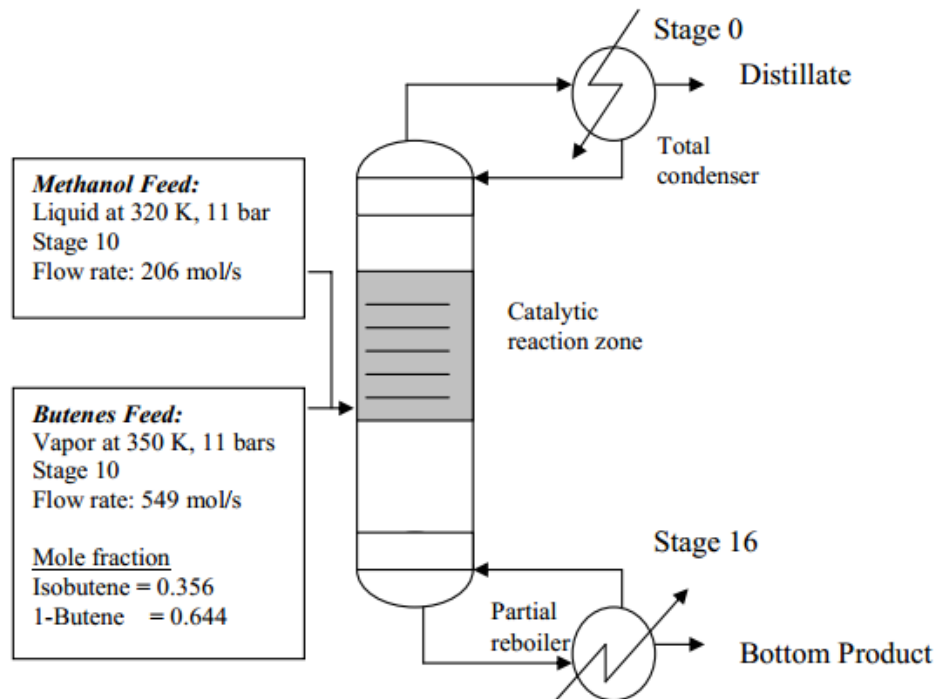


Figure 4: Column Configuration and Feed Specifications for MTBE synthesis (Murat et al., 2003)

3.1.1. Assumptions of Modelling

In this modelling, it was assumed that MTBE synthesis system only consists of main components, namely methanol, isobutylene, MTBE, and n-butene. However, in the actual situation, there are totally a minimum of 12 components with reactive components of methanol, isobutene and MTBE involve in the MTBE synthesis. Moreover, the inert C4 components can be assumed to be represented by n-butene since they have quite similar physical and chemical properties. The small quantities of by-products can be regarded as negligible.

3.1.2. Conditions of MTBE Synthesis

It is assumed that the production rate of MTBE to be 197 mol/s or 500,000 metric tons/year. 6400 kg of catalyst is used for 8 reactive trays with amount of 800kg catalyst each reactive tray. The reactive trays are located in the middle of column from the stage 3 until stage 10. There are totally 17 stages with condenser as stage 0 and partial reboiler as stage 16. The operating pressure is 11 bar or 10.87 atm. The reflux ratio is set to 7. There are two feed streams, methanol feed stream and mixed butenes feed stream with a small stoichiometric excess of methanol. (Nijhuis, Kerkhof, & Mak, 1993)

The feed synthesis specifications, column configuration and operating conditions for MTBE synthesis are summarized in the table below:

Table 1: The feed specifications of methanol and butenes & operating conditions for MTBE synthesis (Nijhuis et al., 1993)

Feed Streams	Methanol	Butenes	Units
Feed rate	206	549	mol/s
Phase	Liquid	Vapour	
Temperature	320	350	K
Pressure	11	11	bar
Feed stage	10	10	
x^{MeOH}	1.0	0.000	
x^{IB}	0.0	0.356	
$x^{\text{n-butene}}$	0.0	0.644	
Number of Stages, N	17		
Column Pressure, P	11		bar
Catalyst Weight, W	6400		kg
Reflux Ratio, r	7		
Bottom Flow, B	197		mol/s

3.2 Procedure of RD Modelling using MOSAIC

The process of RD modelling by using MOSAIC can be summarized by flowchart as shown below:

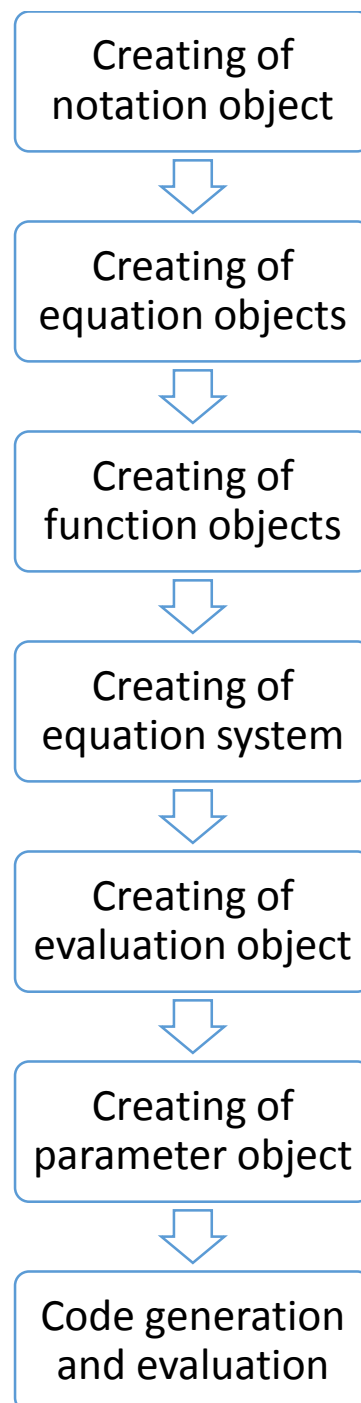


Figure 5: Procedure of modelling using MOSAIC